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Transparent and Electrically Conductive Carbon Nanotube– Polymer Nanocomposite Materials for Electrostatic Charge Dissipation

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Abstract—In recent years, nanocomposite materials have been extensively studied because of their superior electrical, magnetic, and optical properties and large number of possible applications that range from nano-electronics, specialty coatings, electromagnetic shielding, and drug delivery. The aim of the present work is to study the electrical and optical properties of carbon nanotube(CNT)-polymer nanocomposite materials for electrostatic charge dissipation. Single and multi-wall carbon nanotubes were grown by catalytic chemical vapor deposition (CCVD) on

metal/metal oxide catalytic systems using acetylene or other hydrocarbon feedstocks. After the purification process, in which amorphous carbon and non-carbon impurities were removed, the nanotubes were functionalized with carboxylic acid groups in order to achieve a good dispersion in water and various other solvents. The carbon nanostructures were analyzed, both before and after functionalization by several analytical techniques, including microscopy, Raman spectroscopy, and X-Ray photoelectron spectroscopy. Solvent dispersed nanotubes were mixed (1 to 7 wt %) into acrylic polymers by sonication and allowed to dry into 25 μm thick films. The electrical and optical properties of the films were analyzed as a function of the nanotubes' concentration. A reduction in electrical resistivity, up to six orders of magnitude, was measured as the nanotubes' concentration in the polymeric films increased, while optical transparency remained 85 % or higher relative to acrylic films without nanotubes.

I. INTRODUCTION

Carbon nanotubes (CNTs) are among the most studied materials in recent years. Their discovery by Iijima [1] opened a new research direction in nanostructured materials and nanocomposite materials. Their exceptional electrical, mechanical and optical properties make the CNTs ideal materials for applications ranging from sensors, antennas, energy storage mediums, field emitters, supra-capacitors, and nanocomposite materials with improved electrical, optical, mechanical and magnetic properties [2].

A number of studies [3,4] have focused on modifying the surface of CNTs in order to use them in polymer or ceramic nanocomposite materials. The first studies involved intense mechanical mixing [5]; however, since then, the efforts have been focused on chemically changing the nanotubes by adding functional groups (functionalize) for a good dispersion in the polymer matrix. A major challenge is to significantly reduce both the bulk as well as the surface electrical resistivity of the polymer/CNT nanocomposites and at the same time keep the optical transparency at a value higher than 85% to 90 %. The optical absorbance of the polymer/CNT material that can be produced as thin films can be tuned by choosing polymers that have high optical transparency to different ranges of the visible spectra. A major challenge is to generate thin, electrically conductive, and flexible films that remain optically transparent for the visible radiation. Such films can be used for photovoltaic devices, sensors, electrodes, or other applications in nanoelectronics, and optics. The main goal of this work is to study the dispersion of multi-wall CNTs into acrylic polymers, and the formation of thin, optically transparent films with high electrical conductivity. For this study high purity carbon nanotubes grown from acetylene on a Fe:Co:CaCO₃ catalyst system as shown before [6,7] and a commercially available water based acrylic polymer were used.

II. THEORETICAL DISCUSSIONS

A. Carbon Nanotubes

CNTs can be visualized by rolling a one-atom-thick graphite layer into a seamless cylinder. They can consist of one tube of graphite, called single-walled nanotubes (SWNTs), or a number of concentric tubes (cylinders inside other cylinders), called multi-walled nanotubes (MWNTs). The diameter of the SWNTs vary [8,9], depending upon the method that is used to produce them. The orientation of the graphite sheet (a hexagonal lattice of carbon atoms) relative to the axis of the tube determines three types of nanotubes; armchair, chiral and zigzag nanotubes, with strong effects on the electrical properties of these nanotubes. The chiral vector of the nanotube C_h , is defined by $C_h = n\hat{a}_1 + m\hat{a}_2$, where n and m are integers and \hat{a}_1 and \hat{a}_2 are unit vectors in the two-dimensional graphene sheet. The angle between C_h and the unit vector \hat{a}_1 is called the chiral angle (θ). Nanotube structures depend on the values of n, m and θ . Armchair nanotubes are formed when $n = m$ and the chiral angle is 30° , zigzag nanotubes are formed when either n or m are zero and the chiral angle is 0° . The rest of the nanotubes ($0 < \theta < 30^\circ$), are known as chiral nanotubes. Nanotubes' electrical properties depend on their diameter, length, and chirality and nanotubes can be metallic or semiconducting depending on n and m values. MWNTs have a predominantly metallic character. Mixed with different polymeric materials, the CNTs were shown to generate mechanically strong and electrically conductive composites.

B. Raman Spectroscopy and Raman Spectroscopy for Carbon Nanotubes

A laser beam excites the sample and the two types of scattered radiation, elastic and inelastic are examined using a Raman spectrometer. In elastic or Rayleigh scattering, there is no exchange of energy between the photons and the molecules, hence the scattered photons have the same frequency as the incident photons. On the other side, in inelastic or Raman scattering there is an exchange of energy between the photons and the molecules; hence the scattered photons have a different frequency from the incident photons. When the molecule gains energy from a photon, the frequency of the scattered photon is less than the frequency of the incident photon (Stokes scattering). On the other hand, when a molecule loses energy from a photon, the frequency of the scattered photon is higher than the frequency of the incident photon (anti-Stokes scattering). Raman spectroscopy provides significant information about the chemical composition, bonding, molecular structure, phase, localization, and size of different samples. This is an important technique used to analyze and characterize different types of materials being used in a wide range of applications including pharmaceuticals, polymers, thin films, semiconductors, minerals and nanostructured materials including CNTs. For CNTs [10,11], there are only a few vibrational modes that are excited by Raman scattering. Vibrational modes observed for Raman scattering in CNTs are the Radial Breathing Mode

(RBM), the disorder-induced D band, the tangential G band, and the G' band. One of the most important characteristics in the Raman spectrum of SWNTs is the radial breathing mode, which is usually observed between 100 and 250 cm^{-1} and is highly sensitive to the nanotube diameter and therefore is used to identify the nanotube geometry. Since the MWNTs are an assembly of concentric single walls with increasing diameters, the outer tubes with larger diameters make it difficult to differentiate the Raman signal of MWNTs from that of graphite. Therefore the RBM is usually observable in the Raman spectra of MWNTs.

Another feature observed in the Raman spectrum of CNTs is the D band. The disorder-induced D band is usually detected in the frequency range between 1330 and 1360 cm^{-1} and is highly dispersive and is observed in sp^2 carbon materials, which contain defects and impurities. The tangential G band is one of the modes also identified in the Raman spectrum of CNTs. This mode is observed in the frequency range between 1550 and 1605 cm^{-1} and it corresponds to the stretching mode of the Carbon-Carbon bond in the graphite plane. The last important mode observed in the Raman spectrum of CNTs is the G' band. This mode is a second-order harmonic of the D band, which is often present near a frequency of 2700 cm^{-1} . The G' band is also highly dispersive and it is usually observed in sp^2 carbon materials without any defects or impurities.

III. EXPERIMENTAL DESIGN

Several methods were used to accurately analyze both CNTs and the polymeric composite materials doped with nanotubes.

A. Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is a thermal analysis technique that analyzes weight changes of a sample as a function of temperature and/or time, under a controlled atmosphere. TGA generally determines polymer degradation temperatures, absorbed moisture content, the amount of noncombustible filler in polymer or composite materials and is used to investigate a variety of products and metal behaviors. For CNTs, TGA provides information on the purity of these materials [12], as well as the presence of other carbon materials, such as amorphous carbon, fullerenes, mixtures of single wall and multi-wall nanotubes. The amount of weight lost during a TGA experiment could also provide information about the composition of a sample. In addition, using TGA, one can obtain information about the sample's thermal stability, oxidation behavior, or the reaction kinetics of materials such as polymers, ceramics, and metals. For the reported work a Mettler Toledo TGA/SDTA851 module was used to evaluate the purity of the nanotubes used in the experiments as well as the thermal stability of the CNT/Polymer composites. The temperature variation that was used for these experiments was from 25 to 850 $^{\circ}\text{C}$ at a heat-

ing rate of 5 °C/min in air. The sample was placed into a 70 μ l alumina crucible and weighted by a thermobalance at room temperature. The thermobalance, after placed into a high temperature furnace, constantly monitors changes in sample weight as heat is applied to the sample.

B. Raman Spectroscopy and X-ray Photoelectron Spectroscopy

Raman Spectroscopy was performed at room temperature using the Jobin Yvon Horiba LabRAM HR 800 Micro Raman Spectrometer with a resolution of 0.3 cm^{-1} at 680nm. The spectrometer is based on silver treated concave mirrors to ensure optimum spectrograph focus from 400nm to 1600nm and has two different grating systems of 600 and 1800 gr/mm mounted on an automated turret driven by software. The analysis of the CNT samples as well as the CNT/polymer films was done with a 633 nm laser. Spectra were recorded on a range of 100 to 4000 cm^{-1} . The functional groups were analyzed by using the Sun Microsystems of the Kratos XPS instrument.

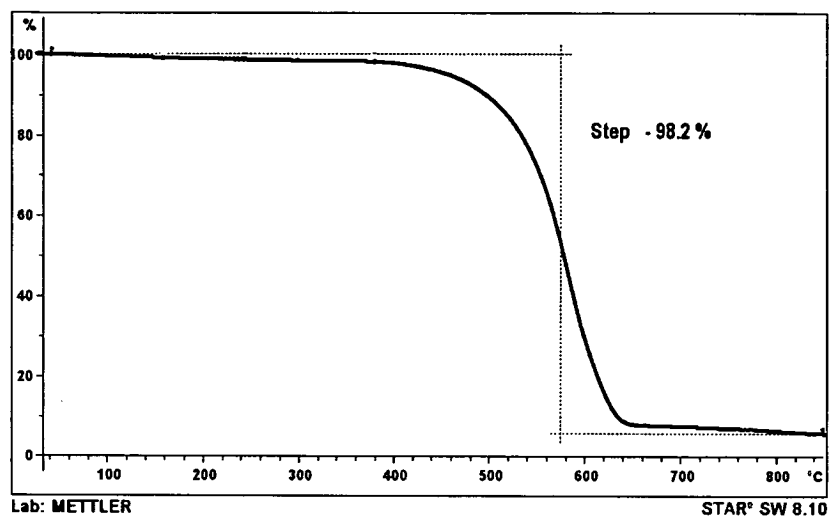
C. Electrical Resistivity Measurements and Electrostatic Charge

Dissipation Measurements

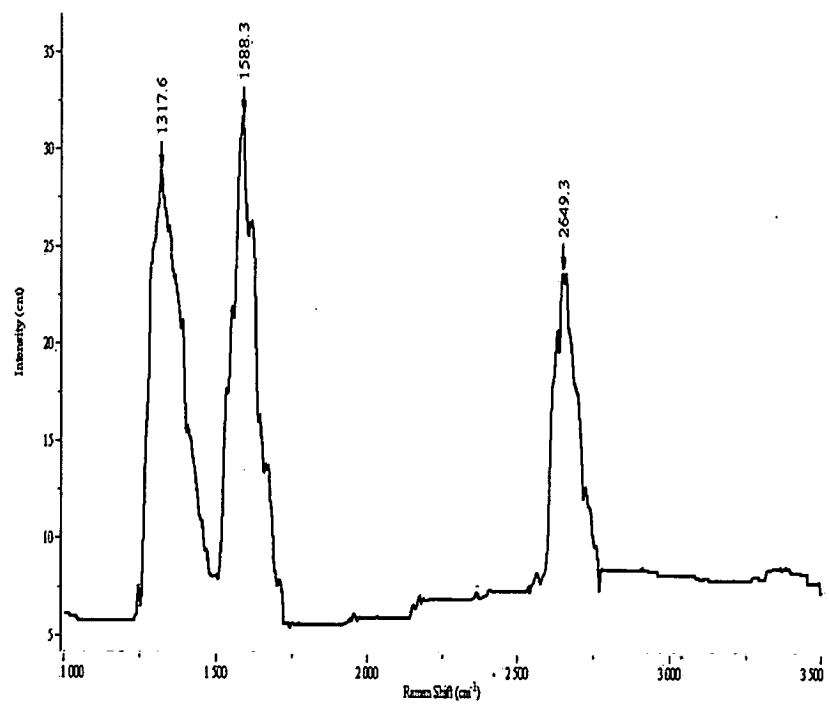
The electrical resistivity analysis of the CNT/ Polymer films was done by Keithley 8009 Resistivity Test Fixture, connected to a high sensitivity Keithley 6517A electrometer. The films were mounted between the two plates of the instrument and a 30 V potential difference was applied to the two sides of the films. The dissipation of the electrostatic charge was performed as previously described [13,14].

IV. EXPERIMENTAL RESULTS AND DISCUSSIONS

High quality MWNTs were synthesized by Catalytic Chemical Vapor Deposition (CCVD) from acetylene and methane on a Fe:Co:CaCO₃ catalyst system, as previously shown [6,7]. After purification, the purity of the nanotubes was over 98 %, as shown in Fig.1a. No significant amounts of amorphous carbon (below 0.08 wt %) were detected in the nanotubes samples, as can be seen from Fig. 1a. The Raman Spectra collected with a 633 nm laser for the multi-wall CNTs is shown in Fig.1b. The Raman spectrum indicates an extremely high crystalline sample, with little structural defects. The well-crystallized walls can be seen in Fig. 1c from the high-resolution transmission electron microscopy (HR-TEM) pictures.



a)



b)



Fig. 1. Thermo Gravimetical Analysis (TGA) of the purified multiwall carbon nanotubes grown on a Fe:Co:CaCO₃ catalyst system from acetylene (a), the corresponding 633 nm Raman spectra (b), and a high resolution Transmission Electron Microscopy picture of a multiwall carbon nanotube (c).

The nanotubes were functionalized with carboxylic acid groups, as previously reported [15]. XPS was used to determine the presence of the functional groups of the walls of the nanotubes, and the results are shown in Table 1. For the peak fitting, five peaks were assigned following similar previous analysis by Ago *et al.* [15]. The main peak consists of both sp²-hybridized graphite-like carbon atoms and carbon-hydrogen bonds. The second peak is assigned to sp³-hybridized carbon atoms as in diamond-like carbon. The final three peaks are associated with carbon-oxygen bonding, typically assigned C-O (alcohol, ether), C=O (ketone, aldehyde), and O-C=O (carboxylic acid, ester) [15,16]. The data showed an increase in the sp³-carbon peak, with a corresponding reduction in the sp²-carbon peak, and an overall increase in the C-O, C=O, and O-C=O peaks. The fitting to the carboxylic O-C=O peak was complicated by the asymmetric long tail peak in the higher energy region of the carbon peak which is typical of graphitic samples [15], and will have slightly higher errors than for the other peaks. However, the data obtained is consistent with that found by Ago *et al.* [15] for treated MWNT.

TABLE 1: CURVE FITTING ANALYSIS OF THE C1s XPS
PEAK SPECTRA

Sample	sp ²	sp ³	C-O	C=O	O-C=O
Untreated	67.4	13.8	13.6	3.2	1.7
Carboxylic treated	61.0	16.5	15.7	4.4	2.4

The functionalized nanotubes were dispersed by extensive sonication into water and mixed in different concentrations with the solubilized acrylic polymers from the class of poly(methyl methacrylate) (PMMA). These polymers are mechanically strong, have good electrical and heat resistance, good weatherability and excellent optical clarity. The mixtures were further sonicated in order to ensure a good dispersion of the nanotubes and the liquid mixture was allowed to form and dry into thin films. The volume of liquid polymer poured into pre-molded cavities was used to control the thickness of the final films. Fig. 2 shows two identical films, one without nanotubes and the other one with 5 wt. % multi wall carbon nanotubes. It can be observed the good dispersion of the nanotubes in the polymeric films and no agglomerations were detected optically.



Fig. 2. Polymeric films without and with 5 wt. % carbon nanotubes. It can be observed the optical transparency for both films.

The bulk electrical resistivity values for films doped with 0 to 7 wt. % MWNTs relative to the values of the acrylic films without any nanotubes is shown in Fig. 3. An exponential decrease of the electrical bulk resistivity of

these films can be observed as the concentration of the nanotubes increases. When nanotubes were further added at values of over 10 wt. % to the polymers, it was noticed a decrease of their dispersion in the polymers and nanotubes were forming agglomerations and the corresponding films were not considered for optical or electrical measurements.

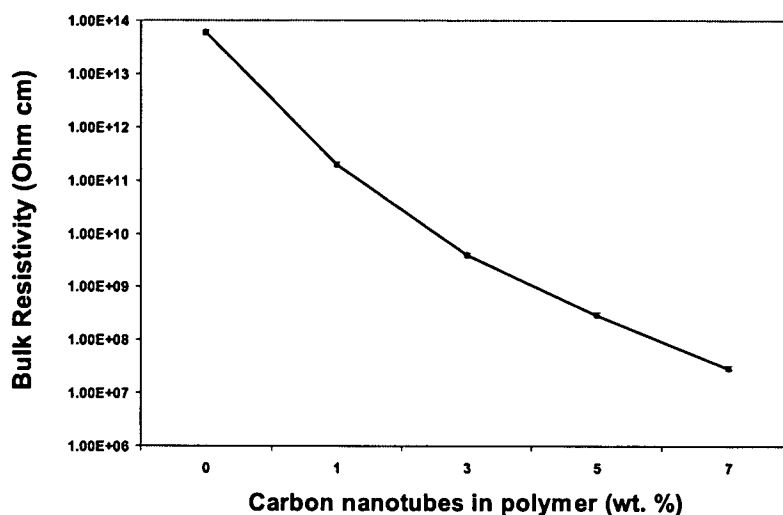


Fig. 3. The decrease in the bulk resistivity of the polymer films at different concentrations of multi-wall carbon nanotubes.

The results shown in Fig. 3, can be explained based on the electrical properties of the CNTs and their electron structure. As mentioned before, similar to graphite sheets, CNTs are composed of sp^2 bonds. Such a bond employs sp^2 orbitals, which are a product of the hybridization of an s orbital and two p orbitals and therefore there are two types of covalent bonds between atoms, sigma and weaker pi ones. This is caused by the p orbitals overlapping less due to their parallel orientation in pi bonds. In graphite sheets, the carbon atoms are sp^2 hybridized and have an unhybridized p orbital, which transports pi electrons through the molecule. Pi bonds are delocalized and they can be shared over the entire molecule. The free p orbitals, which are perpendicular to the plane of the carbon ring, are sometimes compared to delocalized electrons in metallic bonds. The delocalization of the pi bonds and the confinement of electrons normal to the nanotube axis, provide nanotubes with almost perfect unidirectional electrical properties. These delocalized pi electrons are responsible for the increase of the electrical resistivity for the composite materials that contain such nanostructures.

The charge dissipation properties of these films were analyzed based on previously described methods [13,14]. Electrostatic charge was deposited on the surface of the films by using a corona gun and an electrostatic voltmeter placed at a distance of 1 cm in front of the films analyzed the decay of the static charge of the films. The results are shown in Fig. 4. It is observed that the polymer films doped with 5 wt. % CNTs have a much faster dissipation of the electrostatic compared with the acrylic films. Therefore, by introducing small quantities of multi-wall CNTs in the polymeric matrix, the films have become more electrically conductive and therefore have dissipated the static charge at a faster rate. Such nanocomposite materials can be used for applications where fast static charge dissipation is required.

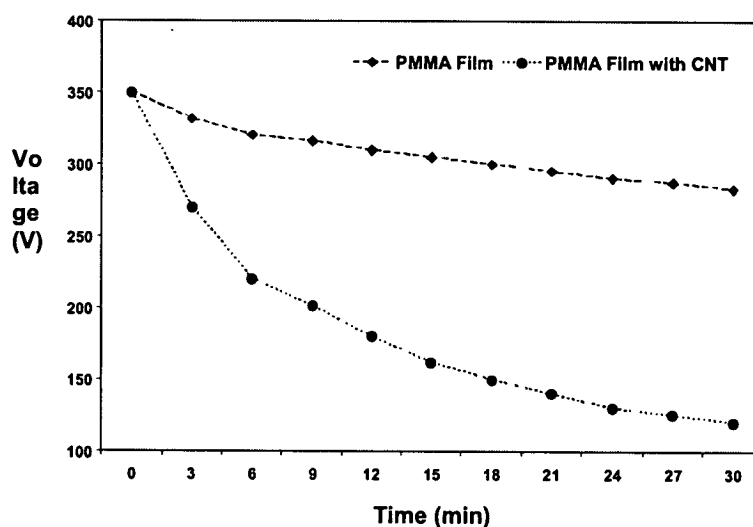


Fig. 4. Charge decay properties of PMMA films and PMMA films doped with 5 wt. % multi-wall carbon nanotubes.

V. CONCLUSIONS

High purity and high crystalline CNTs were mixed in water-soluble PMMA polymers which were formed into films with a thickness of approximately 50 μm . The dispersion of the nanotubes in the polymer films was analyzed by monitoring their optical and electrical properties. As the amount of nanotubes mixed in the polymers increased from 0 to 7 wt. %, a six order of magnitude decrease in the resistivity of the composite films was recorded and the static charge deposited on the films was found to decay significantly faster. A number of applications can be found for such materials in nanoelectronics as

charge and heat dissipaters, in spatial research, and in optical waveguides to name a few.

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